



## Synthesis and Characterization of Magnetic Sponge Nanocomposite for Cleaning Archeological Lime Stone



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**S**PONGE-like magnetic nanocomposite consisting of magnetic nanoparticles  $\text{Fe}_3\text{O}_4$  associated with a polyacrylamide gel matrix has been synthesized and can be used as an active nanomagnetic container for water-based detergent formulations as oil-in-water microemulsions. This prepared system was applied for gentle, controlled and selective cleaning of the archeological lime stone from iron rust and undesired residues. The embedding of magnetic nanoparticles  $\text{Fe}_3\text{O}_4$  into the gel matrix was proved by IR spectroscopy and scanning electron microscopy SEM, showing that the magnetic nanoparticles were successfully embedded in the gel structure. The lime stone samples with corrosion stains were cleaned using the prepared magnetic sponge nanocomposite carrying the water based detergent, followed by characterization of the surface of the samples before and after treatment through SEM, X-ray Florescence XRF and colour measurements. SEM images confirmed the full removal of stains. XRF analysis detected decreasing of the iron oxide ratio from 10.62% to 0.26% after cleaning. The colour measurement recorded the colour changes of the samples' surface before applying of the iron rust and after treatment with the prepared cleaning system and it was that the colour changes were with acceptable ratio and cannot be visible by naked eye.

**Keywords:** Polyacrylamide, Nanocomposite, o/w microemulsion, Nanomagnetic sponge, Archeological lime stone.

### Introduction

Polymeric nanocomposites have much attention in the recent years and play a vital rule in the preparation of functional materials. They composed of polymer matrix combined with inorganic nanoparticles. [1-5] The size and properties of polymers make them a convenient scaffold to disperse and arrange other nanoparticles to produce nanocomposites with enhanced properties. In particular, nanocomposites consisting of a polymeric network as gel that embeds the nanoparticles to form nanocomposite gels have much attention to overcome the limitations of the mechanical properties of conventional polymeric hydrogels.[6-8]

Magnetic nanocomposites have attracted increasing attention due to their unique physicochemical properties for a variety of industrial

applications [9, 10]. Magnetic nanocomposites are based on magnetic nanoparticle or nanorods/nanowires/ nanowhiskers embedded inside a matrix of a porous network structure, a sheet structure or dense bulk materials. Especially, nanocomposite of magnetic polymer hydrogel involving magnetic nanoparticles (MagNPs) represents a feasible approach in the preparation of magnetic gels to combine the peculiar properties of both hydrogels and MagNPs in the formulation of smart functional materials [11].

Polymeric hydrogels consist of a three-dimensional polymer network and are produced by the reaction between a polymer and crosslinker usually free-radical copolymerization of acrylamide (AM)-based monomers with a chemical crosslinker, such as N,N'-methylene bisacrylamide, in an aqueous solution. These hydrogels have extensive number of applications

for their unique properties. In these applications, the molecular constitution of the hydrogels and their elastic and softness properties is critical. [12-16]

Recently, several types of physical gels have been developed to be applied in the field of culture heritage to clean surfaces for art conservation and restoration. The gelated cleaning system is very versatile and is considered a highly selective, controlled and gentle agent and it is preferred to the cleaning with organic solvent, because it acts only on the deleterious layers, without penetration of the solvent into the artifact that done with using neat organic solvents causing damage chemically or mechanically the surface to be cleaned, and do not leave residues on the surface after removal of the cleaning agents. Gels decrease the capillary and solvent evaporation because it is immobilized within the gel network Therefore, it is possible to achieve good selectivity in the removal of dirt, varnishes, corrosion and aged adhesives.[17-22]

The nanomagnetic gel acts as a smart nanocomposite materials and represents the most advanced and versatile system for cleaning and will have a dramatic impact on the conventional methods used in the conservation field and in several other fields that achieve high selectivity and control where fine tuning of the release or uptake of confined material is required.[17] The polyacrylamide hydrogel was applied in the conservation of Easel Paintings in the removal of synthetic adhesives from lined canvas without leaving any gel residues.[23] Microemulsions and gels were applied for the conservation of cultural heritage.[24] Also, the microemulsion was applied before as cleaning fluid by using paper pulps – cotton fiber – wood mulch. [25]

The present work is concerned in synthesis of magnetic hydrogel nanocomposite consists of magnetic nanoparticles that were embedded in a polyethylene glycol-polyacrylamide gel matrix and its application as an active sponge-like nanomagnetic container for water-based detergent system as oil-in-water microemulsions for cleaning of archeological lime stone from iron corrosion stains.

#### Materials

Acrylamide was from ALPHA CHEMIKA Mumbi-INDIA, N,N'-methylene bisacrylamide was get from MERCK-Schucharai Bei Munchen. Magnetite nanoparticles  $\text{Fe}_3\text{O}_4$  with particle size approximately 20 nm was supplied

from nanocomposix company-4878 Ronson-SanDiego-USA. Polyethylene glycol PEG ( $M_w \approx 300$  g/mol) was purchased from Loba chemie. Maleic anhydride (MA). Ammonium persulfate (APS; BDH laboratory Supplies Poole, BH15 1TD). Texapon N70 sodium lauryl ether sulfate SLES was from o-BASF Co. German. 2-butanone (methyl ethyl ketone MEK) was purchased from pubchem.

#### Experiments

##### *Nanomagnetic Gel Synthesis.*

Firstly, the magnetic polyethylene glycol PEG-derivative was synthesized to help the MagNPs to be embedded inside the acrylamide gel structure. It was prepared as follows, 100ml of chloroform was deoxygenated through Argon purging for 15 min. 10 grams of Polyethylene glycol ( $M_w \approx 300$  g/mol) was added together with 9.8 g of maleic anhydride MA under Argon. The reaction was then carried out in the dark for 24 h at 37 °C. During the reaction, two ester bonds are formed as a result of the chemical reaction between the anhydride group of MA and the hydroxyl groups of PEG to obtain the product as MA-PEG-MA.

A stable magnetic fluid at concentration as 1% w/w was prepared by dispersing positively charged  $\text{Fe}_3\text{O}_4$  nanoparticles in water (referred to as FF). A solution of MA-PEG-MA was prepared by dissolving 0.5 g in 10 mL of water. This solution was then added to the magnetic fluid (5 mL, 0.5g of MagNP). In this step, the carboxylic groups react with the surface of the nanoparticles to form as lightly viscous magnetic fluid. [8,26] Separately, a solution containing 0.75 g of acrylamide and 60 mg of N,N'-methylene bisacrylamide in 10 mL of water was prepared. The acrylamide solution and magnetic fluid were then purged with  $\text{N}_2$  and mixed together. Ammonium persulfate was then added as a radical initiator, and the polymerization reaction was carried out at 42 °C for 4h. At the end of the polymerization, a magnetic black gel is obtained Mag Gel.

A blank gel containing no MagNPs was prepared as well and it is slightly opalescent. Only in the case of gel prepared without stirring, phase separation was observed, with one fluid phase on top containing nonmagnetic particles and a gel-phase on the bottom containing almost the totality of magnetic particles. The produced magnetic gel was characterized using Scanning electron microscope SEM and Infrared spectroscopy IR.

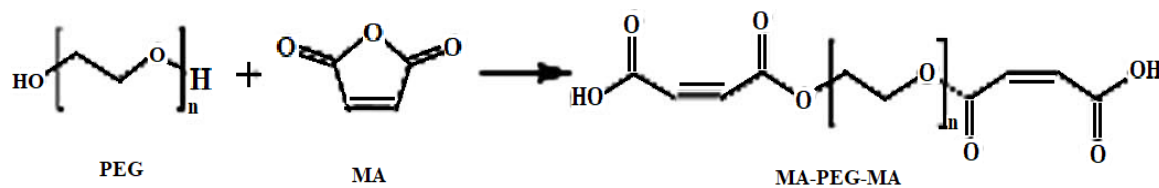


Fig. 1. Scheme of the esterification reaction between ethylene glycol PEG and maleic anhydride MA.

#### MagGel loading

The prepared magnetic gel was loaded by a ternary oil in water microemulsion as detergent system which composed of texapon N70 as surfactant, 1-butanol as co-surfactant, methyl ethyl ketone MEK organic solvent as oil phase and water in a ratio as 4.35%, 7%, 13.55% and 75.1%, respectively. [27, 28]

#### Lime stone samples preparation

All the lime stone fragments were collected from Hoosh Elbasha (Misr Elkadima), all samples were cut in cubic form (10\*10\*4 cm).

Iron rust stains were applied to samples by using iron salt in powder state and then industrial obsolescence for 21 days under 150 °C was carried out. The samples were divided into two groups (A & B), where group A was untreated while group B was cleaned by the prepared magnetic sponge carrying the o/w detergent microemulsion using compress technique for 45 min for each sample.

#### Characterization:

##### Scanning electronic microscope SEM

The surface morphology of the samples studied were examined by scanning electron microscope (SEM) using a QUANTA FEG250 model- Japan for high-resolution imaging and composition analysis. The specimens for SEM observation were prepared by cutting a small size and carefully affixed to a SEM stub. Each specimen was gold-coated using a sputtering device before being observed under the SEM. [29].

##### IR spectroscopy

The characteristic beaks of the prepared magnetic gel were determined by using FTIR spectroscopy (JASCO-FT/IR-6100) in the range of 4000–400  $\text{cm}^{-1}$  using KBr powder. Each sample was mixed with KBr and placed in a Drift cell. [30]

##### X-Ray Florescence (XRF)

XRF analysis of the untreated and cleaned lime stone samples were carried out. Pellets of stone samples were prepared and analyzed using XRF machine of Brucker. [31].

#### Color measurement

The CIE-Lab values of lime stone samples (untreated and cleaned by magnetic gel) were measured by using a double beam Optimatch spectrophotometer (Datacolor international Spectraflash SF450-UK). When the colour in different formulae was desirable to express colour specifications in terms of such correlates. The colours that were given in CIE Lab coordinates were , L value corresponding to the brightness (100 = white, and 0 = black), while  $a^*$  value to the red–green coordinate (positive sign = red, and negative sign = green), and  $b^*$  value to the yellow–blue coordinate (positive sign = yellow, and negative sign = blue). The total difference of colour  $\Delta E^*$  between two colour stimuli  $\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}$  [32].

#### Results & Discussion

The sponge like nanomagnetic composite was formed from cross linking the magnetic nanoparticles with a polymer network based on acrylamide. To cross link the particles, a PEG-based polymer was prepared through the esterification of polyethylene glycol with maleic anhydride (MA). The resulting MA-PEG-MA molecules consist of carboxylic groups at both ends of the PEG chain. The binding reaction between magnetic nanoparticles and carboxylic acids act as a complete coupling of the carboxylic head group over the surface of the magnetic nanoparticles. So, MA-PEG-MA was directly reacted with the magnetic nanoparticles, forming a slightly viscous magnetic fluid. After polymerization of acrylamide in the presence of the magnetic fluid, the magnetic nanoparticles were embedded inside the gel structure through the reaction of double bonds of acrylamide with the double bond of MA-PEG-MA. [17] As the sponge was considered as a tightly bonded structure, the produced nanomagnetic gel was hard enough to be handled. That enables the gel to be suitable for various applications. The prepared nanomagnetic gel was characterized by scanning electronic microscopy SEM and IR Spectroscopy.

### Scanning Electronic Microscopy SEM

SEM images for blank gel (A) and magnetic gel (B) are shown in Figure (2) at different magnifications. The brightest parts in the images may refer to the MagNPs which are very electron-rich. These aggregates of nanoparticle may also appear as the irregular shape, while the darker gray areas with a smooth surface may refer to the pure gel (less electron-rich) and it was shown that the magnetic nanoparticles were successfully and homogeneously embedded in the gel structure. The SEM image showed that the structure is very porous with different pore size distributions (pores with micron and nano-size distributions) that enables this material to be used as an active sponge-like nanomagnetic container for other substances as water-based formulations as oil-in-water microemulsions..[17]

### IR Spectroscopy

IR-spectra of the gel and magnetic gel nano-composite were obtained in order to identify the characteristic infrared peaks of the polymer and the nanoparticles (Figure 3). The large broad band at  $3439\text{ cm}^{-1}$  is ascribed to the O-H stretching vibration in OH - groups. The absorption peaks around  $1631\text{ cm}^{-1}$ ,  $1515\text{ cm}^{-1}$  are due to the asymmetric and symmetric bending vibration of C=O. [33] The band below  $700\text{ cm}^{-1}$  can be assigned Fe-O stretching mode. The band corresponding to Fe-O stretching mode of  $\text{Fe}_3\text{O}_4$  can be seen at  $626\text{ cm}^{-1}$  in the IR spectra (b) for the magnetic gel [34]. But it was also noted in the gel spectra (a) with little migration, so, there is no large different characteristic band.

### Iron Corrosion Stains removal

After applying the prepared magnetic sponge carrying the water-based detergent microemulsion

in the cleaning of the iron corrosion stains on the surface of archeological lime stone, the lime stone samples surface were characterized before and after treatment via SEM, XRF and color change measurement.

### Scanning Electron Microscope (SEM):

The surface of the experimental samples was examined by SEM before and after cleaning the iron corrosion stains using the prepared magnetic gel MagGel. Through SEM images investigation, it was illustrated in figure (4) for the iron corrosion stains on the surface of the experimental samples before cleaning, we can note calcification layers of rust on the surface between the crystals and stone, also notes fill the pores and voids between crystals of stone by impurities resulting from steel. After cleaning, it was seen that, in case of cleaning by MagGel, a large proportion of rust stains after removing the poultice and the completion of the cleaning process, and the ineffectiveness of the boat to get rid of spots and removed stains fully. [24]

### X-Ray Florescence (XRF)

By analyzing the iron corrosion stains on the surfaces of experimental samples by XRF before and after the cleaning, it was found that the percentage of rust before applying the cleaning materials was 10.62%. However, after the application of the prepared MagGel loaded with the detergent fluid and remove the poultice, we found that for the surface which has been cleaned by MagGel, the percentage of iron oxide was reduced to 0.26%, which confirms the effectiveness of the MagGel in the removal of iron corrosion stains from the surface of lime stone samples.[8]

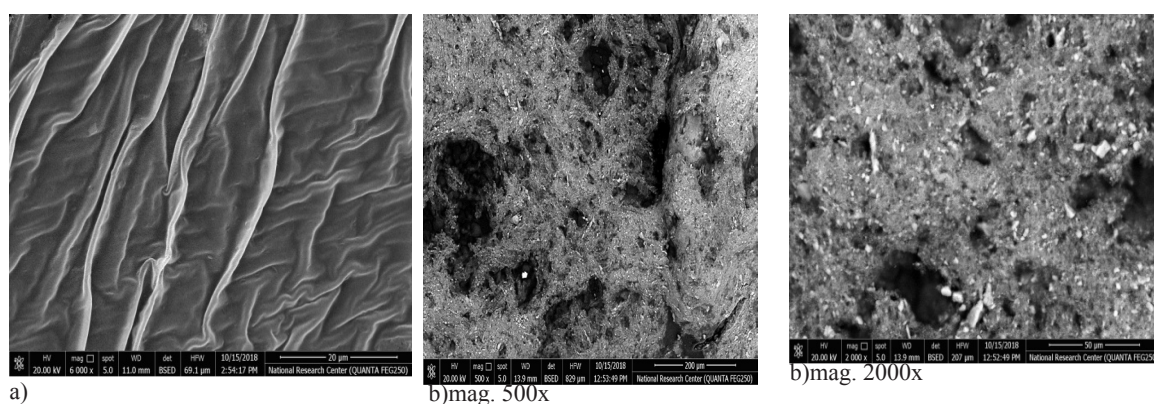


Fig. 2. SEM micrographs of the neat gel (a) and MagGel sample at different magnifications (b).

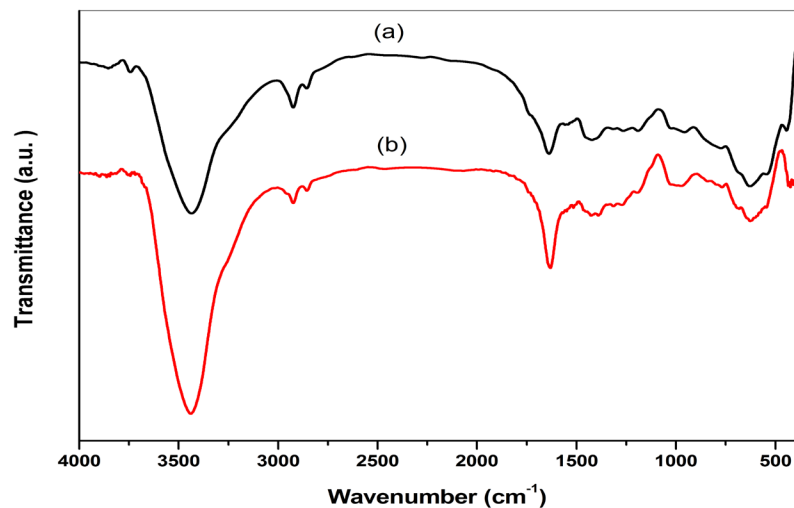


Fig. 3. IR-spectra of the gel (a) and magnetic gel nanocomposite (b).

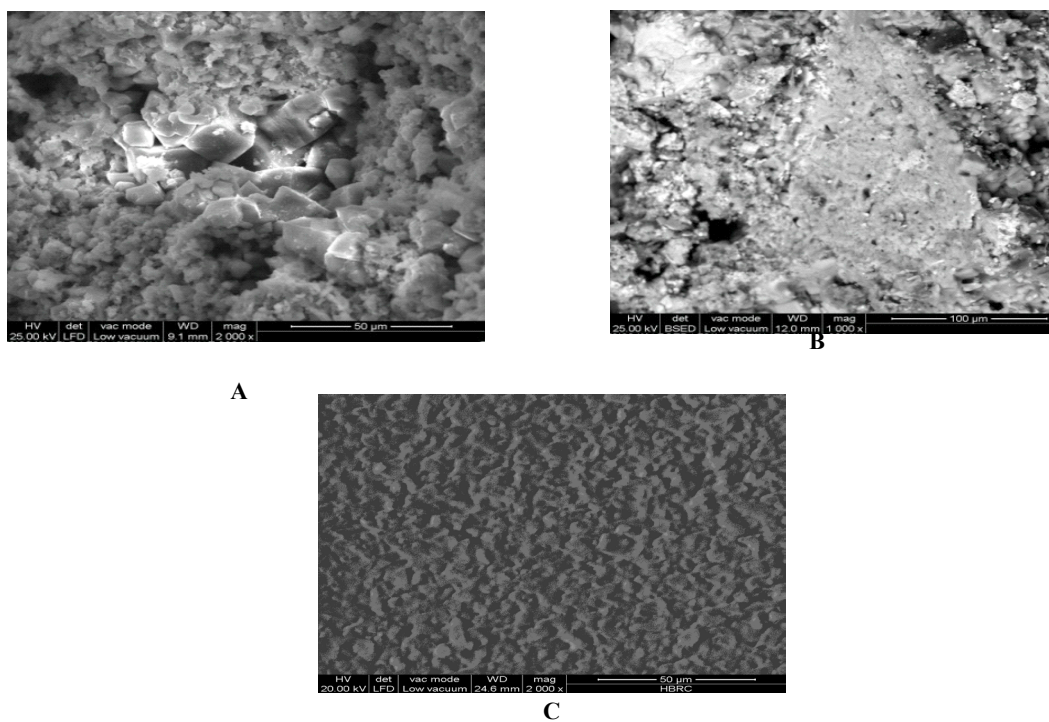


Fig.4. SEM of lime stone A) Before iron corrosion stains applied B) After iron corrosion stains applied. C) After cleaning by using polymer.

TABLE 1. XRF of lime stone samples stained by iron corrosion before and after cleaning.

Oxide %	AL <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	SiO <sub>2</sub>
Before cleaning	0.17	42.7	10.62	0.038	0.3	1.61	1.63
After cleaning by polymer	0.3	42.55	0.2	0.07	1.4	2.21	4.33

**TABLE 2. Colour change percentage of the samples after iron stain corrosion removal and comparing the standard sample.**

	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E$
Iron corrosion stained samples	- 46.15	8.61	4.22	47.14
Sample after cleaning by polymer	-5.41	1.01	4.29	6.98

*Surface colorimetric change*

It was determined by measuring the colour change percentage on the surface of lime stone samples after the application of the cleaning system to remove the surface stains, and comparing the results to a particular standard stone surface which was measured before applying stain patches, in order to determine the extent of the colour change that had occurred in the overall appearance of the surface before and after the application of surface stains and cleaning system.

Surface colorimetric change was measurement by taking three readings per sample to calculate the values of ( $\Delta L$ ,  $\Delta a$ ,  $\Delta b$ .) to know the differences of colour between the samples and its counterpart with the standard sample, then calculate  $\Delta E$  to determine the difference final color change that occurred between the samples before after cleaning as the following :  $\Delta E = \{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\}^{1/2}$  [30]

In accordance with the international standards for tests of the colour change, the  $\Delta E$  value must be  $<5$ , and through the above table it is clear that the values of  $\Delta E$  for samples after applying a spot of iron corrosion rust on the surface and after a statute of Industrial obsolescence was (47.14), which shows the big change wrought by iron corrosion rust on the surface of the stone. However, after the application of the prepared water-based detergent MagGel system to remove the rust stains from the investigated samples. It was found that this prepared cleaning system provided effective results in reaching the surface to the required extent colour change when compared to the sampling standard. Although, the value of  $\Delta E$  was 6.98 where it had slightly exceeded the permissible limits according to the international standards, but the change was acceptable and not significant and cannot be visible by naked eye. [25, 35- 37]

**Conclusion**

Magnetic nanocomposite sponge consisting of magnetic nanoparticles associated with a polyacrylamide gel matrix have been

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synthesized and was used as an active sponge-like nanomagnetic container for water-based formulations as oil-in-water detergent microemulsion. This magnetic sponge system was applied to the control and selective cleaning of archeological lime stone with corrosion stains. This aqueous cleaning is preferred to cleaning with organic solvent, because it offers advantage of selective and gentle removal of hydrosoluble and hydrophobic materials (aged adhesives) and less aggressive to artifact's materials. IR spectroscopy and scanning electron microscopy SEM showed the successful embedding of the magnetic nanoparticles homogeneously in the gel structure. The lime stone with iron corrosion stain artifacts were treated with this prepared water based magnetic sponge system and their surface were characterized before and after treatment through SEM images, XR-Florescence analysis and the colour measurement. Where it was shown the effectiveness of the prepared magnetic gel in removal of the iron corrosion stains with no penetration of the solvent.

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